

Thermal stability of cathodic-arc amorphous hard carbon films studied by NEXAFS, Raman spectroscopy, and nanoindentation

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INTRODUCTION

Amorphous hard carbon films have properties which are of great interest and importance for a number of tribological and protective applications. They are very hard, chemically inert, have a low coefficient of friction, and are very smooth. They consist of a random structure of sp^2 and sp^3 bonded carbon atoms. It has been that a carbon ion energy of about 100 eV is the optimum condition to produce films with the highest sp^3 fraction. The sp^3 fraction can reach up to 85% [1], the mass density up to 3.0 g/cm³ [2], and the hardness up to 95 GPa [3]. If a magnetic macroparticle filter is used, the films are very smooth and free of macroparticles, the surface roughness can be as low as <0.1 nm rms and a few tens of a nanometer peak-to-valley [4].

Many properties of cathodic arc deposited films have been studied in great detail, but little is known about the thermal stability of these films. It was found that elevated temperature of the films during deposition leads to a more graphitic character of the films, whereas cooling of the substrate during deposition leads to films with a higher sp^3 content [3]. McKenzie et al. [2] investigated cathodic arc deposited films with and without nitrogen doping during annealing in vacuum for 1 hour up to 700°C. They observed very little change in the plasmon energy of about 29.5 for films during the heat treatment from which they concluded a stable thermal behavior.

We found in earlier measurements that -100V substrate bias leads to the highest sp^3 fraction (85%) of the deposited films [1]. In a study of the thermal stability of cathodic arc deposited films in air using Raman spectroscopy and nanoindentation [5] we found that films deposited at no bias or at a bias of -500V or higher are stable up to 200°C. For higher temperatures the films graphitize as indicated by the Raman spectra, and above 400°C a considerable loss of film thickness occurs due to oxidation. Films deposited at -100V showed a constant Raman spectrum for temperatures up to 500°C, but they start to oxidize for temperatures above 450°C. Due to complete loss of the films at 550°C (the initial film thickness was 450 nm) we could not observe their thermal behavior at higher temperatures in air, whereas the present study with annealing in vacuum allows it.

EXPERIMENTAL

The samples were deposited on silicon substrates at -100V bias (for maximum sp^3 content) using a cathodic-arc plasma source combined with a 90 degrees bent magnetic macroparticle filter. The source and filter are described in detail elsewhere [6]. The film thickness was 70 nm. Samples were annealed in vacuum (base pressure $p=5 \times 10^{-8}$ Pa, up to 5×10^{-6} Pa during annealing) at temperatures from 300-850 °C; the annealing time was 15 minutes.

NEXAFS spectroscopy at the carbon K edge was performed at beamline 9.3.1. of the ALS. The energy resolution of this beamline at the carbon K edge is about 0.15 eV. The samples were mounted at an angle of 54.7° to the incident X-rays; this is the "magic angle" which eliminates the dependence of the p and s states on the polarization of the X-ray source [7]. Figure 1 shows the carbon K edge NEXAFS spectra in the total electron yield mode for the cathodic arc deposited carbon sample heated to different temperatures. For comparison there is also shown a spectrum of highly oriented pyrolytic graphite. The spectra of the deposited carbon are typical diamond-like spectra, with the π^* antibonding state resonance located at 284.9 eV and the broad σ^* shape resonance around 300 eV [8-10]. The spectra remain essentially unchanged up to a temperature of 700°C. For 800 and 850°C heating temperature the spectra change and the graphite exciton peak appears at 292 eV.

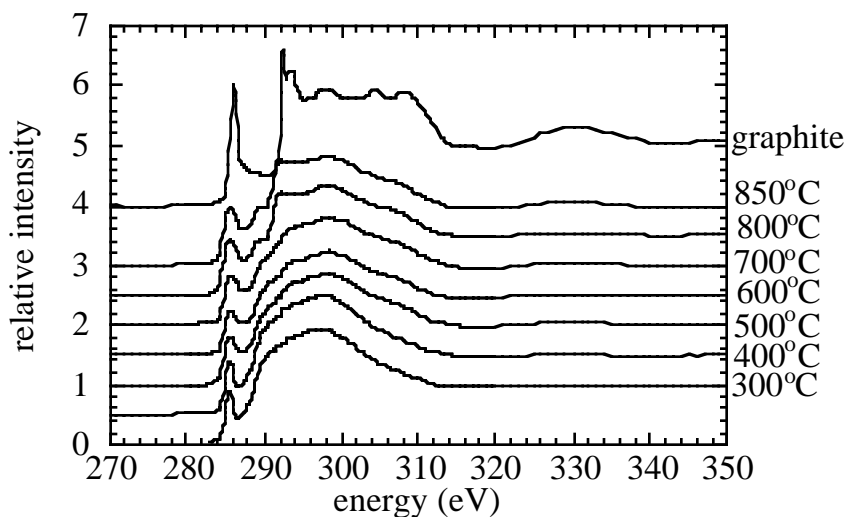


Fig. 1: NEXAFS carbon K edge spectra of cathodic arc deposited amorphous hard carbon film heated at different temperatures in UHV. A weak graphitic exciton peak appears at 292 eV at annealing temperatures of 800 and 850 °C.

Raman spectroscopy was performed on the same sample before and after heating to 850°C in vacuum. Raman spectra were obtained using 10 mW of 476 nm laser light. The spot size was ca. 20 microns and the integration time was 3 minutes. The Raman spectrum of cathodic-arc deposited films is a single, broad, asymmetric feature centered at ca. 1550 cm^{-1} (G-band). The peak center of this feature was determined by the zero-crossing of the differentiated spectrum. The precision of this procedure, as determined by repeat measurements on the same film, is $\pm 2 \text{ cm}^{-1}$. The Raman spectrum is only slightly changed after the heat treatment; a very small shoulder around 1350 cm^{-1} indicates the appearance of the graphitic D-band.

Nanoindentation was performed using a Hysitron nanoindenter. The hardness and elastic modulus of the cathodic arc film were determined before and after annealing to 850°C. It was found that the hardness as well as the elastic modulus are very high (about 90 GPa and 400 GPa, respectively) and are not changed by the heat treatment.

DISCUSSION

The NEXAFS results show a stable film structure up to 700°C and a modification (graphitization) of the film above 700°C whereas the Raman spectra are changed only very slightly, and

nanindentation measurements show constant film properties up to 850°C. This discrepancy can be explained by the surface sensitivity of NEXAFS whereas Raman spectroscopy and nanindentation integrate over the whole film thickness (70 nm). The sensitivity of NEXAFS is given by the electron escape depth which is typically about 5 nm [11] whereas the Raman spectrum collects the scattered light from a depth of about 200 nm given by the absorption coefficient of the film. Nanoindentation measures the hardness and elastic modulus as a function of the contact depth, and can further be influenced by the substrate.

CONCLUSIONS

The study has shown that amorphous hard carbon films formed by cathodic arc deposition using a pulsed substrate bias of - 100V are thermally very stable. Heating in vacuum up to 850°C modifies (graphitizes) only the surface layer whereas bulk properties such as hardness and elastic modulus remain stable. Up to 700°C heating in vacuum no change in the film properties was observed.

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